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Thermodynamic Properties of Technetium and Rhenium Compounds. I. Vapor Pressures of Technetium Heptoxide, Pertechnic Acid and Aqueous Solutions of Pertechnic Acid[1,2]

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Vapor pressures of technetium heptoxide, pertechnic acid and of saturated aqueous solutions of the latter compound were determined using a glass differential Bourdon gage. The vapor pressures between 25 and 260° followed a two-term equation: $\log p\,(\text{mm.}) = A/T + B$, with values for A of −7205, −3571, −2395 and −2375, and for B of 18.28, 8.999, 8.207 and 8.201 for Tc_2O_7(c), Tc_2O_7(l), $HTcO_4$(c) and $HTcO_4$(sat.), respectively. Values for enthalpy, entropy and standard free energy changes in the fusion, vaporization, sublimation and solvation of these compounds were estimated and compared with corresponding quantities for analogous rhenium compounds. In general, the properties of technetium and analogous rhenium compounds were closely similar as expected from their positions in the Periodic Table.

The thermodynamic properties of the various compounds of the synthetic element, technetium, are of interest by reason of the fact that a knowledge of them will contribute in an important way to a unified understanding of the chemistry of Group VIIB of the Periodic Table. The work to be reported in the present paper accordingly has dealt with the measurement of the vapor pressures of Tc_2O_7 and of $HTcO_4$ and its aqueous solutions in order that enthalpies and entropies of sublimation, vaporization, fusion and other thermochemical quantities might be estimated. It has been instructive to compare these thermodynamic quantities with those derived from recent measurements on rhenium heptoxide and perrhenic acid[4] using similar vapor pressure techniques. The preparation and some of the properties of technetium heptoxide and pertechnic acid have been reported.[5] Experience has indicated that the former compound is stable up to its boiling point temperature.

Experimental

Vapor pressure measurements were conducted with an all-glass differential Bourdon gage,[6] since Tc_2O_7, like rhenium heptoxide, was found to attack both mercury and stopcock grease. Pure technetium metal, contained in a tube sealed onto a receiving bulb of the gage, was burned in dry oxygen at 500–600°. Subsequently, about 200 mg. of the resulting anhydrous Tc_2O_7 was sublimed into the evacuated gage which was then sealed off from the combustion tube. The gage was suspended vertically on a rigid frame, and was immersed in a silicone-oil thermostat-bath,[7] which could be regulated to within ±0.2° in the range from below room temperature up to 260°. Jacket pressures necessary to "balance the gage" (*i.e.*, to return the index to its zero point) were supplied from a 20-liter reservoir fitted with a three-way stopcock to permit the gradual admission or withdrawal of air from the system. Absolute pressures were read with a cathetometer on a closed-tube mercury manometer connected to the jacket. The gage sensitivity was about 1 mm. of index displacement per mm. pressure differential. Because of the unexpectedly low vapor pressures exerted by solid Tc_2O_7, it was also necessary to use the gage as a manometer. This was done by reading the displacement between the index, or movable pointer of the gage, and the stationary reference pointer with a traveling microscope. Calibrations with a McLeod gage showed these displacements to be linear with pressure for deflections as great as 2–3 mm. Zero point corrections were determined by cooling the gage to ice temperatures, and then finding the pressure necessary to attain a "balance." Pressures were estimated to ±0.05 mm. for liquid Tc_2O_7 and to ±0.005 mm. for the solid compound. Zero point corrections were negligibly small for all pressures except those exerted by solid Tc_2O_7. In this latter case uncertainties in the magnitudes of these corrections can easily introduce errors of from 10 to 30% in the absolute corrected pressures. The data are given in Tables I and II.

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(1) Presented before the Division of Physical and Inorganic Chemistry, 121st National Meeting, American Chemical Society, Buffalo, N. Y., March 23–27, 1952.

(2) This work was performed for the Atomic Energy Commission.

(3) This paper is based on a thesis by James W. Cobble presented to the University of Tennessee in partial fulfillment of requirements for the Ph.D. degree, June, 1952.

(4) Wm. T. Smith, Jr., L. E. Line and W. A. Bell, THIS JOURNAL, **74**, 4964 (1952).

(5) G. E. Boyd, J. W. Cobble, C. M. Nelson and W. T. Smith, Jr., *ibid.*, **74**, 556 (1952).

(6) T. E. Phipps, M. L. Spealman and T. G. Cooke, *J. Chem. Ed.*, **12**, 321 (1935).

(7) Silicone-oil, DC-550, Dow-Corning Corp., Midland, Michigan. *p*-Aminophenol was added to prevent polymerization at higher temperatures.

TABLE I

THE VAPOR PRESSURE OF SOLID TECHNETIUM HEPTOXIDE

$T^a_{\text{cor.}}$	P^b_{obs}	P_{cor}	T^a_{cor}	P^b_{obs}	P_{cor}
391.2	0.995	0.65	377.9	0.555	0.18
388.7	.700	.46	373.2	.415	.095
387.7	.660	.42	368.5	.240[c]	.05
384.1	.720	.36	362.2	.300	.03
378.5	.400[c]	.215			

[a] Degrees absolute. [b] Millimeters of mercury. [c] Pressures so indicated obtained on cooling.

TABLE II

THE VAPOR PRESSURE OF LIQUID TECHNETIUM HEPTOXIDE

T^a_{cor}	P^b_{obs}	P^c_{cor}	T^a_{cor}	P^b_{obs}	P^c_{cor}
393.3[c]	0.50	1.0	489.7	54.10	54.6
413.1	1.60	2.1	503.0	82.40	82.9[d]
427.5	3.50	4.0[d]	512.5	107.35	107.8
441.0	6.80	7.3	519.5	132.90	133.4[d]
446.4	9.10	9.6	521.5	141.40	141.9[d]
459.8	16.20	16.7[d]	524.5	153.60	154.1
473.8	28.50	29.0	529.4	176.70	177.2
483.5	42.40	42.9[d]			

[a] Degrees absolute. [b] Millimeters of mercury. [c] Triple point. [d] Pressures so indicated obtained on cooling.

Vapor pressures of anhydrous $HTcO_4$ and of its saturated aqueous solution were measured in a second Bourdon gage. This compound was prepared *in situ* by distilling technetium heptoxide into the lower part of the gage, and then letting water vapor enter the vacuum line. Excess water was then removed by gentle heating and evacuation. Samples prepared in this manner contained excess Tc_2O_7, but enough pertechnic acid was also present to allow the measurement of the vapor pressure of water formed by its equilibrium dissociation. Saturated aqueous solutions were produced by subsequently allowing these crystals to absorb excess water, after which the system was sealed-off under vacuum.

Equilibrium pressures seemed to be attained rapidly in all systems except with the saturated pertechnic acid solution where approximately two hours was required to obtain constancy at each temperature. Proof that equilibrium pressures were being registered was supplied by demonstrating that measurements taken in either heating or cooling sequences were consistent with one another within the experimental precision (Fig. 1).

Qualitative electric conductivity measurements were performed on both solid and liquid Tc_2O_7 and Re_2O_7 by determining the direct current resistance of a small, sealed glass cell containing two bright tungsten wire electrodes which dipped into approximately 100 mg. of the compounds distilled into the cell. This apparatus was tested by similar measurements on fused, anhydrous $ZnCl_2$, a known electric conductor.

Experimental Results and Discussion

A plot of the logarithm of the vapor pressure of technetium heptoxide against the reciprocal of the absolute temperature is given in Fig. 1 along with similar plots for rhenium heptoxide. The method of least squares was applied to obtain the best straight line relation for each equilibrium. For the solid this was

$$\log p_{(\text{mm.})} = -7205/T + 18.279 \qquad (1)$$

with a probable error of ±8%, while for the liquid

$$\log p_{(\text{mm.})} = -3571/T + 8.999 \qquad (2)$$

with a probable error of ±1%. The calculated melting point from the simultaneous solution of eq. 1 and 2 was 118.4° which is in fair agreement with the value, 119.5 ± 0.1°, from direct observations.[5] The boiling point temperature from eq. 2 was 310.6°. This estimate, however, may be uncertain by as much as ±2°, for vapor pressure measurements were conducted only up to 255.5°.

The comparison afforded by Fig. 1 of the vapor pressures of technetium and rhenium heptoxides is of interest by reason of the differences between these closely analogous compounds. Perhaps the most surprising observations were the low melting point of Tc_2O_7 and the relatively wide range in temperature over which this compound remained a liquid. Further, the entropy of fusion calculated from the above equations appeared to be unreasonable. Values for the other thermodynamic functions, however (Table III), reveal that Tc_2O_7 is otherwise quite like Re_2O_7. An explanation[8] for this apparently high entropy of fusion can be found by assuming reasonable values for the heat capacities of the solid, liquid and gas[9] and thereby estimating ΔC_p values for the transitions. Using 6 cal. g.-atom^{-1} deg.$^{-1}$ for the solid, 7 cal. g.-atom^{-1} deg.$^{-1}$ for the liquid and 38 cal. mole^{-1} deg.$^{-1}$ for the gas,[10] ΔC_p becomes −16 for sublimation and −25 for vaporization. This procedure leads to temperature dependent enthalpies of the form $\Delta H^0 = \Delta H_0{}^0 + \Delta C_p T$: $\Delta H^0{}_{(\text{vap})} = 28{,}650 - 25T$ and $\Delta H^0{}_{(\text{subl})} = 36{,}450 - 16T$. The modified vapor pressure equations then become

$$(\text{solid–vapor}) \log P_{(\text{mm.})} = \frac{-7969}{T} - 8.07 \log T + 41.11 \qquad (3)$$

$$(\text{liquid–vapor}) \log P_{(\text{mm.})} = \frac{-6264}{T} - 12.59 \log T + 48.38 \qquad (4)$$

The accuracy of the experimental data is not sufficiently high to distinguish between these equations and those given previously; further, the calculated boiling and melting points are not appreciably changed.

TABLE III

THERMODYNAMIC PROPERTIES OF TECHNETIUM AND RHENIUM HEPTOXIDES

	Tc_2O_7	Re_2O_7[a]
$\Delta F^{\circ}{}_{\text{subl}}$, cal. mole^{-1}	$32{,}950 - 70.4T$	$33{,}500 - 55.6T$
$\Delta F^{\circ}{}_{\text{vap}}$	$16{,}330 - 28.0T$	$17{,}700 - 28.0T$
$\Delta F^{\circ}{}_{\text{fus}}$	$16{,}620 - 42.4T$	$15{,}810 - 27.6T$
ΔH_{fus}, kcal. mole^{-1}	16.6 ± 0.5	15.8 ± 0.1
ΔH_{vap}	16.3 ± 0.2	17.7 ± 0.1

[a] Estimated from data of Smith, Line and Bell, ref. 4.

However, these values for the enthalpies now lead to much more reasonable values for the entropies. Thus the entropy of vaporization becomes 24 e.u. at the boiling point and 48 e.u. at the melting point. Combined with an entropy of sublimation of 77 e.u. at the melting point, the entropy of fusion at this latter temperature (120°) is calculated to be 29 e.u.

Since all of the required C_p values are only estimates, one is not able at the present time to decide upon the validity of this proposed treat-

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[8] The authors are indebted to Professor Leo Brewer for helpful discussions on the treatment of the heats and entropies of fusion.

[9] K. K. Kelley, Bureau of Mines Publication 476 (1949).

[10] This heat capacity for the gaseous molecule corresponds to about $^3/_4$ of the full vibrational excitation; larger values of ΔC_p than those indicated give poorer agreement with the observed vapor pressures.

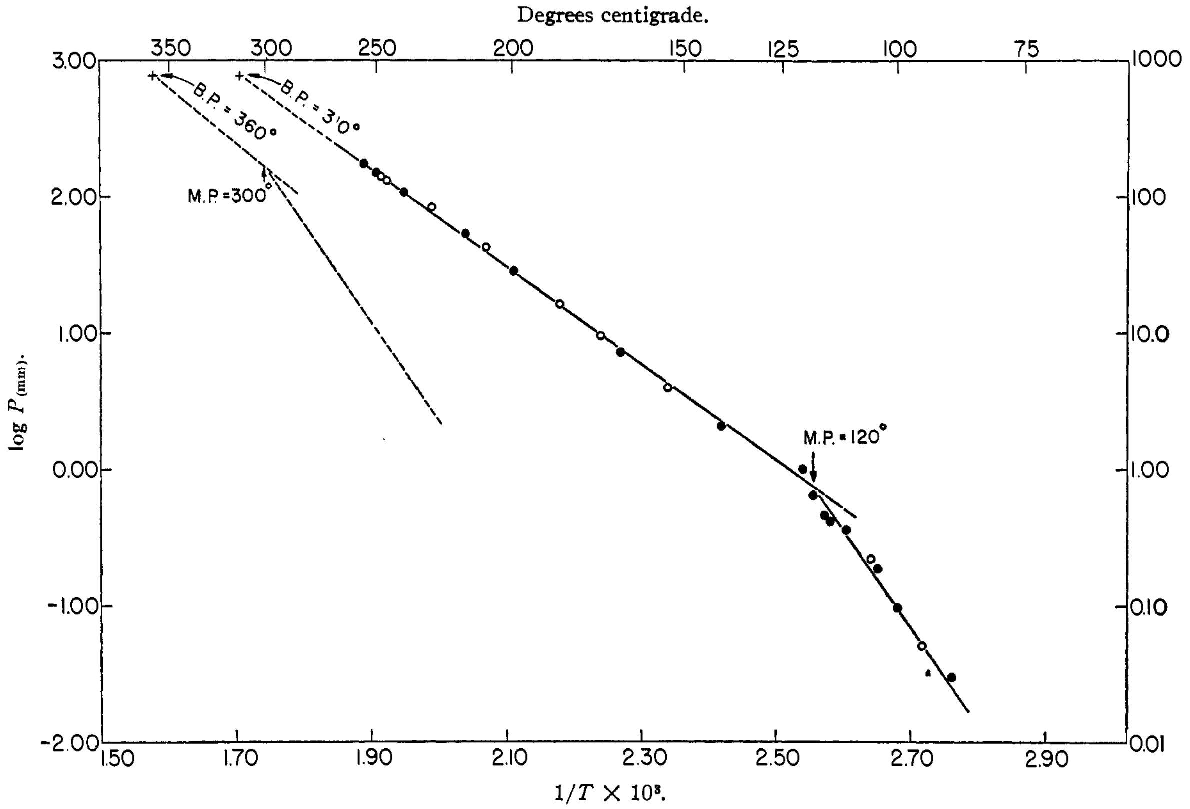

Fig. 1.—Temperature dependence of the vapor pressures of solid and liquid technetium heptoxide: dotted lines, vapor pressures for Re_2O_7 from Smith, Line and Bell, ref. 4; open circles on cooling.

ment, although the general approach is undoubtedly correct. A complete understanding of the situation must, therefore, await calorimetric data on the heat of fusion of Tc_2O_7.

X-Ray diffraction measurements[11] on both Tc_2O_7 and Re_2O_7 have indicated that these two compounds are not isomorphous, and that the former possesses a low symmetry. Another interesting difference is that while solid technetium heptoxide seems to be a fair electrical conductor at temperatures near its melting point, the liquid is not. Rhenium heptoxide exhibits just the opposite behavior.

The measurements of the temperature dependence of the dissociation equilibrium for pertechnic acid

$$HTcO_4(c) = 1/2H_2O(g) + 1/2Tc_2O_7(c) \qquad (5)$$

are shown in Fig. 2 together with the vapor pressures determined on saturated aqueous pertechnic acid solution. The data for the dissociation could be fitted to within ±1% by the equation

$$\log p_{(\text{mm.})} = -2395/T + 8.207 \qquad (6)$$

A comparison of the data in Figs. 1 and 2 will readily show that the contribution of the partial pressure of $Tc_2O_7(c)$ to the total dissociation pressure of pertechnic acid was negligibly small between 20 and 90°.

It may be seen (Fig. 2) that pertechnic acid dissociates more readily than perrhenic acid to form heptoxide and water. Further, it is apparent that the evaporation of *acidic* Tc(VII) solutions soon yields the anhydrous oxide, while continued heating at 100° will lead to the loss of Tc_2O_7 which exerts a vapor pressure of about 0.6 mm. at this temperature.

A quantitative comparison of the solvation reactions of technetium and rhenium heptoxides is afforded by Table IV which lists the enthalpy, entropy and standard free energy changes for eq. 5 and for the analogous dissociation of $HReO_4$ at 25°. The same quantities also have been estimated for the reaction

$$HTcO_4(c) = 1/2H_2O(l) + 1/2Tc_2O_7(c) \qquad (7)$$

using recent selected thermodynamic data for the vaporization of water.[12]

TABLE IV

THERMODYNAMIC DATA FOR THE SOLVATION OF TECHNETIUM AND RHENIUM HEPTOXIDES AT 298.1°K.

Reaction	ΔH, cal.	$\Delta F°$, cal.	ΔS, cal. deg.$^{-1}$
$2HTcO_4(c) = Tc_2O_7(c) + H_2O(g)$	10,950 ± 50	3686 ± 18	24.4 ± 0.2
$2HTcO_4(c) = Tc_2O_7(c) + H_2O(l)$	430 ± 50	1632 ± 18	−4.0 ± .2
$2HReO_4(c) = Re_2O_7(c) + H_2O(g)$	11,020 ± 100	4460 ± 18	22.0 ± .4
$2HReO_4(c) = Re_2O_7(c) + H_2O(l)$	500 ± 100	2418 ± 18	−6.4 ± .4

The experimental data for the vapor pressures of the saturated aqueous pertechnic acid solution obeyed the equation

$$\log p_{(\text{mm.})} = -2375/T + 8.201 \qquad (8)$$

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[11] R. D. Ellison, Chemistry Division, Oak Ridge National Laboratory, to be published.

[12] National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Series I, 1948.

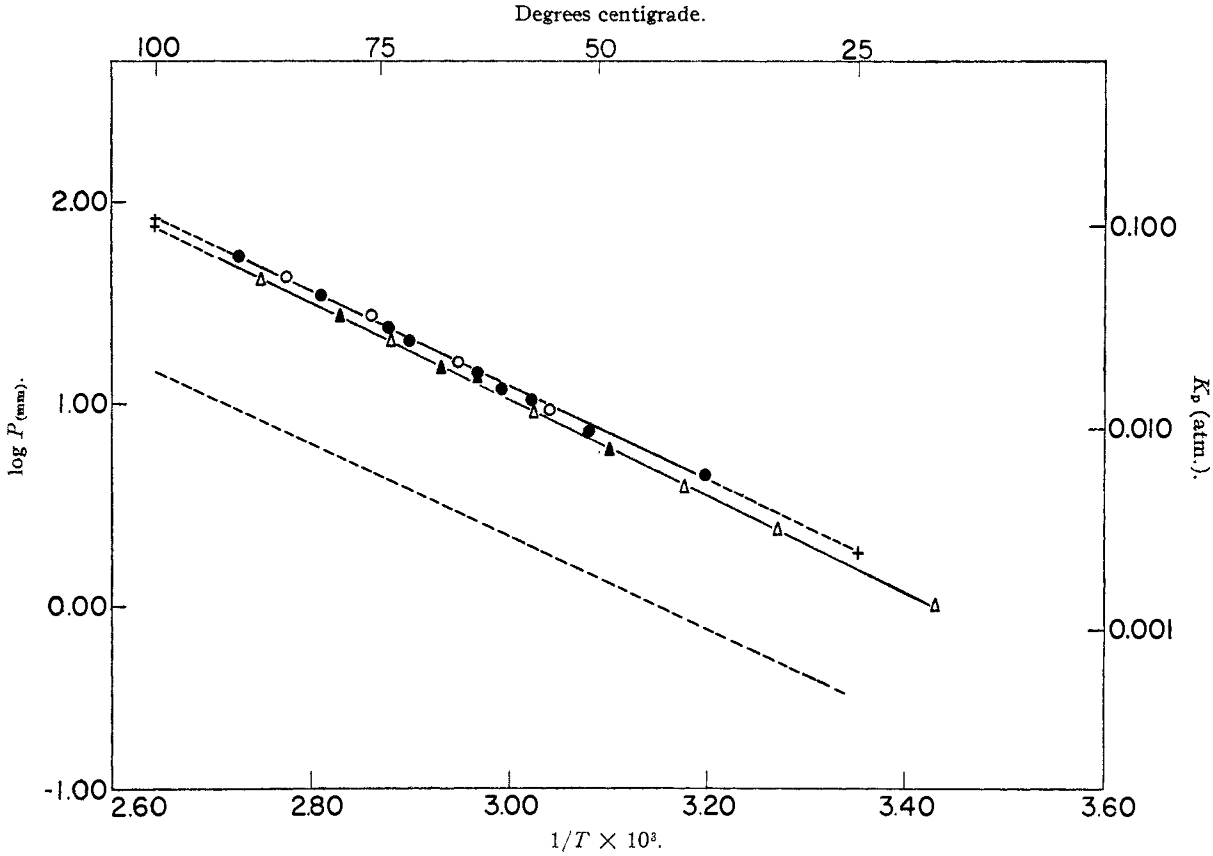

Fig. 2.—Temperature dependence of the vapor pressures of solid $HTcO_4$ and of saturated aqueous solutions of $HTcO_4$ (upper line): dotted line, vapor pressures for $HReO_4(s)$ from Smith, Line and Bell, ref. 4; open symbols on cooling.

with an average deviation of ±2%. The vapor pressures of the saturated solutions are seen (Fig. 2) to be only a few millimeters higher than those for the anhydrous acid. This finding implies that there will be very little difference in the tendency for the two systems to take up additional water. Vapor pressure measurements on saturated aqueous perrhenic acid solutions do not seem to have been reported; presumably here the situation would be very similar to that for pertechnic acid.

The thermodynamic functions at 25° estimated from eq. 8 are

$$H_2O\text{ (satd. soln. }HTcO_4) = H_2O\text{ (g, 1 atm.)} \quad \Delta H = 10{,}860 \pm 100\text{ cal. mole}^{-1} \qquad (9)$$

and

$$H_2O\text{ (satd. soln. }HTcO_4) = H_2O(l) \quad \Delta H = 340 \pm 100\text{ cal. mole}^{-1} \qquad (10)$$

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